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Acidic Anions in PM_{10} Particle Fraction in Zagreb Air, Croatia

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Abstract This paper presents the results of 7 years continuous measurement of acidic anions chlorides, nitrates, and sulphates in PM_{10} particle fraction in the city of Zagreb, Croatia. The mean annual mass concentrations of the investigated anions in PM_{10} particle fraction varied from 0.28 to 0.95 μg/m^3 for chlorides, from 3.21 to 7.87 μg/m^3 for nitrates and from 3.98 to 9.71 μg/m^3 for sulphates. The concentration levels of all measured anions showed significant seasonal differences. The most contributing to the PM_{10} mass were sulphates, then nitrates, and then chlorides. The mobile source emission was an important contributor to particle mass.

Keywords Chlorides · Nitrates · Sulphates · Ion chromatography

Airborne particles with an aerodynamic diameter of less than 10 μm (PM_{10}) are considered as inhalable, and have been found widely associated with health problems, due to their direct effect on lung tissues or indirect effect as carriers of adsorbed toxic substances. They can also influence many atmospheric processes including visibility variations and cloud formation, and play a major rule in acidification of rainfalls and affect climate (Bourotte et al. 2007; Wang and Shooter 2001). The main concern of most air pollution studies is the chemical composition of the particulate matter. The analyses of the airborne particles can provide information about their chemical components, origin and specific emission sources. Characterisation of the aqueous extract of the aerosols shows that the chemicals originating from motor vehicle exhausts, soil dust re-suspension and industry emission, mainly occur in an easily water-soluble form (Fernandez Espinosa et al. 2002; Kyotani and Iwatsyki 2002). Many investigations have shown that, sulphate (SO_4^{2-}), nitrate (NO_3^-), ammonium (NH_4^+) and water-soluble organic carbon are the dominant chemical species of water-soluble matter in aerosol particles (Bourotte et al. 2007; Wang and Shooter 2001; Fosco and Schmeling 2006; Wang et al. 2006; Xiao and Liu 2004).

This paper presents the results of 7 years continuous measurement of major acidic anions chlorides, nitrates, and sulphates in PM_{10} particle fraction in the city of Zagreb, Croatia in relation to their mass concentrations, seasonal variations, relative contribution of measured species to PM_{10} mass and the prediction of the relative importance of pollutant sources.

Materials and Methods

Twenty-four-hour samples of PM_{10} particle fraction were collected in the northern residential part of Zagreb, at the distance of approximately 20 m from the road with moderate to high traffic density. Sampling was carried out continuously for 7 years (21 March 1999–20 March 2006). Samples of PM_{10} particle fraction were collected on cellulose membrane and quartz filters using inertial impactor at the average sampling flow rate of 70 Lpm, from approximately 100 m^3 of ambient air. Filters were dried to constant humidity in a desiccator for 24 h before and after sampling. Particle mass concentration was determined by gravimetry using a Mettler Tolledo MX5 microbalance. After that all the filters were cut into two

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parts. One half of the sampling filter was used to analyze acidic anions.

Samples were extracted from filters using an ultrasonic bath for 1 h at 40°C. The undissolved part was separated by centrifugation. Blank samples (unexposed filters) were used and processed simultaneously with the filed samples. For anion content measurement we used a Dionex-120 ion chromatograph equipped with suppressed conductivity detection, a Dionex AS14: 4 mm Analytical Column and AG14: 4 mm Guard Column. In this investigation, we followed the same sample preparation and procedure, chemical analysis of ionic species and quality assurance as described in our previous publication (Cackovic et al. 2008).

Results and Discussion

Table 1 summarises the statistical parameters: number of samples (N), mean values, standard deviations (SD), median, and range (minimum and maximum values) of mass concentrations of measured pollutants over the entire measuring period.

Results show that mean annual mass concentrations of PM_{10} varied from 33.5 to 41.8 μg/m^3. The mean annual mass concentrations of the investigated anions in PM_{10} particle fraction followed the order chlorides, then nitrates, and then sulphate. Their mass concentrations varied from 0.28 to 0.95 μg/m^3 for chlorides, from 3.21 to 7.87 μg/m^3 for nitrates and from 3.98 to 9.71 μg/m^3 for sulphates.

Seasonal variations of anion mass concentrations in PM_{10} particle fraction are shown in Fig. 1 for chlorides in Fig. 2 for nitrates and in Fig. 3 for sulphates. Results show that the concentration levels of all measured anions showed significant seasonal differences ($p < 0.01$, ANOVA, one-way). Chloride and nitrate values were high in the winter or autumn and lower in the summer, while sulphates did not show a clear seasonal trend.

Table 1 Mass concentration of pollutants (μg/m^3)

Measuring period	Statistical parameters	PM_{10}	Cl^-	NO_3^-	SO_4^{2-}
1999/2000	N	353	360	358	360
	Mean ± SD	41.8 ± 26.8	0.41 ± 0.40	3.56 ± 3.25	5.43 ± 4.65
	Median	36.3	0.30	2.37	4.00
	Range	4.3–221.8	ND–2.92	ND–23.30	0.49–30.22
2000/2001	N	360	365	365	365
	Mean ± SD	35.6 ± 18.8	0.28 ± 0.28	3.25 ± 2.72	4.62 ± 3.30
	Median	31.8	0.22	2.42	3.86
	Range	2.9–106.3	ND–1.80	0.15–20.72	0.37–20.22
2001/2002	N	347	365	365	365
	Mean ± SD	39.4 ± 21.2	0.44 ± 0.41	3.21 ± 2.99	3.98 ± 3.13
	Median	36.6	0.30	2.00	3.11
	Range	5.5–136.3	ND–5.31	0.11–21.01	0.19–20.56
2002/2003	N	323	364	365	364
	Mean ± SD	35.8 ± 23.8	0.43 ± 0.40	5.63 ± 5.34	7.62 ± 6.77
	Median	30.3	0.29	2.00	5.38
	Range	2.6–137.1	0.04–3.40	ND–28.57	0.91–49.84
2003/2004	N	360	342	354	358
	Mean ± SD	33.5 ± 21.5	0.95 ± 0.48	7.87 ± 5.86	9.71 ± 6.19
	Median	29.05	0.85	5.89	8.41
	Range	1.1–119.4	0.11–3.82	0.23–38.73	0.50–41.85
2004/2005	N	363	358	357	357
	Mean ± SD	38.2 ± 26.7	0.47 ± 0.44	4.79 ± 4.40	7.55 ± 6.54
	Median	32.37	0.36	3.27	5.90
	Range	1.6–198.7	ND–4.40	0.51–24.68	0.99–49.87
2005/2006	N	363	339	363	363
	Mean ± SD	40.4 ± 29.5	0.39 ± 0.34	4.48 ± 5.00	6.35 ± 5.81
	Median	31.2	0.21	2.72	4.49
	Range	6.2–199.9	ND–2.57	0.20–34.93	0.42–44.01

ND not detectable

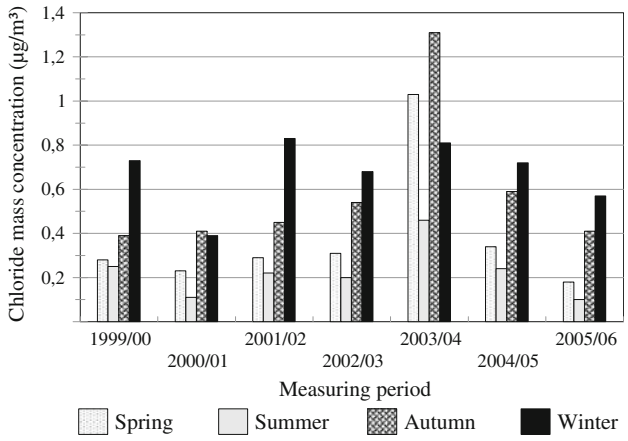

Fig. 1 Seasonal variations of chloride mass concentration

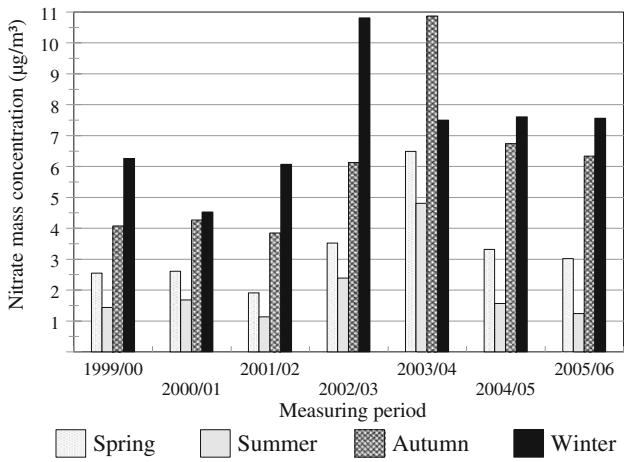

Fig. 2 Seasonal variations of nitrate mass concentration

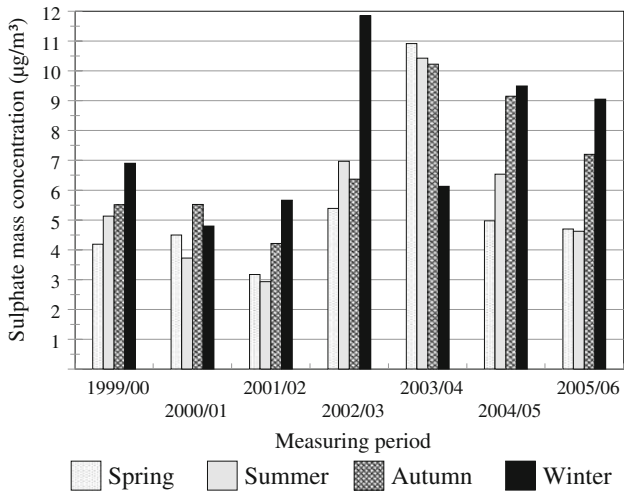

Fig. 3 Seasonal variations of sulphate mass concentration

The high concentration levels of measured pollutants in cooler period may be due to great emissions of pollutants and their precursors from anthropogenic sources, combustion of fossil fuels and motor vehicle exhaust, and meteorological conditions. Particulate nitrate is mainly formed by oxidation of nitrogen oxides (NO_x) to nitric acid, which then forms particles through reaction with sodium chloride or with ammonia. In contrast to the oxidation of SO_2 which always results in the formation of aerosol SO_4^{2-} mass, HNO_3 formed by the oxidation of NO_x is distributed between the gas and aerosol phases (Khoder 2002).

The mass ratio of $(NO_3^-)/(SO_4^{2-})$ is therefore used as an indicator of the relative importance of mobile or stationary sources of sulphur and nitrogen in the atmosphere (Xiao and Liu 2004). Annual average mass ratios of $(NO_3^-)/(SO_4^{2-})$ obtained in PM_{10} (Fig. 4) were in the range from 0.74 to 0.88, respectively, which suggests that mobile source emission was an important contributor to particle mass.

Figure 5 shows anion (chlorides, nitrates and sulphates) mass content (%) in PM_{10} particle fraction over the entire measuring period. The most contributing to the PM_{10} mass were sulphates in the range of 11.47%–25.45%, then nitrates in the range of 9.03%–21.65%, and then chlorides in the range of 0.79%–2.72%.

Seasonal variations of chloride mass content in PM_{10} particle fraction over the entire measuring period are shown in Fig. 6. The same parameters for nitrate and sulphate content in PM_{10} particle fraction are shown in Figs. 7 and 8.

Anion content varied with the season, and the lower values were mainly recorded in the spring for chloride, and in the summer for nitrate. Sulphate content also showed significant seasonal differences with lower values in the winter ($p < 0.01$, ANOVA, one-way).

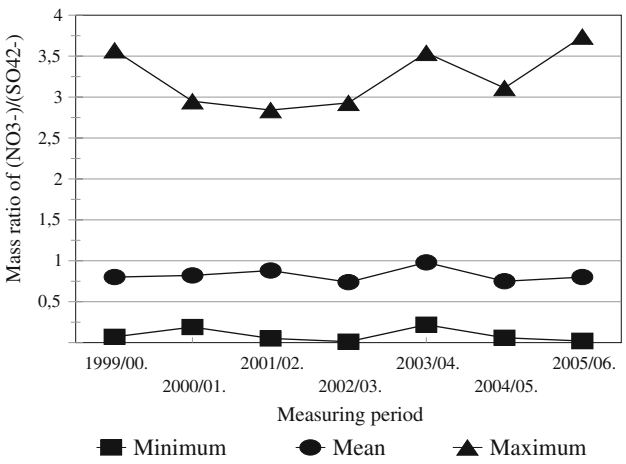

Fig. 4 Mass ratio of $(NO_3^-)/(SO_4^{2-})$

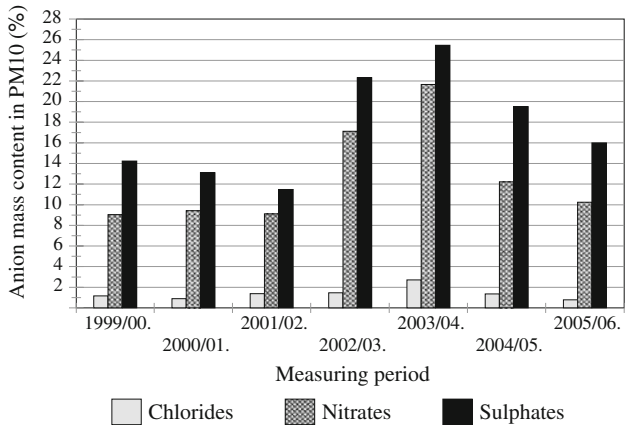

Fig. 5 Anion mass content in PM_{10} mass

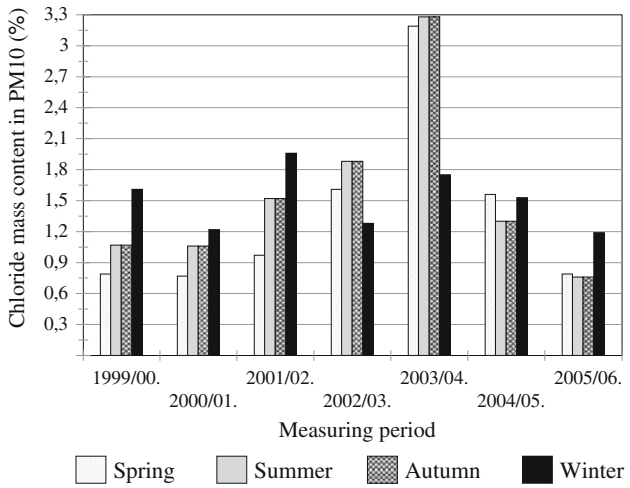

Fig. 6 Seasonal variations of chloride mass content in PM_{10} particle fraction

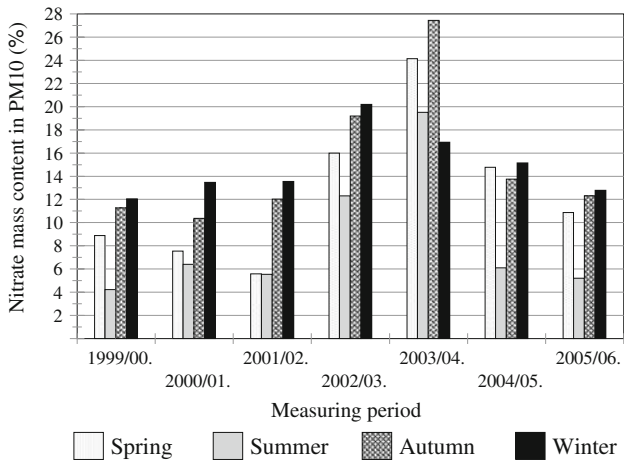

Fig. 7 Seasonal variations of nitrate mass content in PM_{10} particle fraction

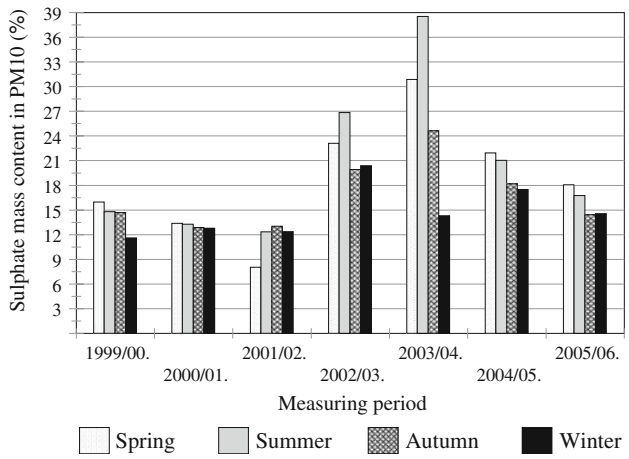

Fig. 8 Seasonal variations of sulphate mass content in PM_{10} particle fraction

Marked seasonal variations of chloride and nitrate content could be attributed to the variation in the volatility of ammonium and sodium salts leading to lower summertime values. The high sulphate content in the summer and autumn may be due to strong solar radiation, and photochemical gas-phase oxidation of gas precursor pollutants. During the winter aqueous-phase oxidation of gas precursor pollutant to secondary aerosols is common (Khoder 2002).

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